Copper(II) carboxylates with 4-aminopyridine: neutral mononuclear structures, isomerism of aceto compounds and a novel tetranuclear structure

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Reactions of copper(II) carboxylates with 4-aminopyridine (4-apy) were investigated and their products structurally characterized by single crystal X-ray diffraction. Reaction of copper(II) acetate resulted in two isomers of a monomeric complex of composition $Cu(ac)_2(4\text{-apy})_2$ with markedly different stabilities: the violet form, **1**, unstable in air and the blue, stable form, **2**. In both isomers the ligands are arranged around the copper atom in a *trans* geometry. The 4-apy ligands lie almost in the plane in **1**, while they are twisted with respect to each other in **2**. Variations were observed also in the coordination of the acetate groups to the copper ion. The energy difference between the two isomers was obtained on the basis of *ab initio* MO calculations. The result agrees well with the observed relative stabilities in the solid state. Monomeric complexes of the same stoichiometry were obtained also by the reaction of Cu(II) hexanoate and heptanoate with 4-apy. The violet $Cu(hex)_2(4\text{-apy})_2$, **3**, and $Cu(hep)_2(4\text{-apy})_2$, **4**, are isostructural and possess *trans* geometry of the ligands around the copper centre. Reaction of 4-apy with Cu(II) octanoate lead to formation of a novel, unprecedented basic centrosymmetric tetranuclear compound of composition $Cu_4(oct)_6(OH)_2(4\text{-apy})_2$, **5**. Complex **5** contains bidentate bridging and monoatomic bridging carboxylate groups, triply bridging hydroxyl groups and 4-aminopyridine as a terminal ligand. In all five compounds 4-apy is coordinated through the endocyclic nitrogen atom only.

Copper(II) carboxylates are structurally a very diverse group of coordination compounds due to the various coordination modes of the carboxylato ligands. In general, most of the compounds contain a tetracarboxylato $Cu_2(OOCR)_4$ core having a typical dimeric paddle-wheel structure. A large number of unligated complexes have been reported, all having the polymeric structure $[Cu_2(OOCR)_4]_n$ in which dimeric units are linked into chains by the interaction of a Cu ion from one unit with the carboxylate oxygen of a neighbouring dimer.[1–3] Unligated copper(II) carboxylates react with additional (in most cases nitrogen and oxygen donor) ligands to form complexes that have been shown to have diverse stereochemistries. By breaking the polymeric structure with the coordination of an additional ligand to the apical position, distinct dimers of the acetate hydrate type are obtained [general formula $Cu_2(OOCR)_4L_2$].[4] These have been subject of many magnetostructural studies.[5] By increasing the ligand concentration, monomeric complexes of $Cu(OOCR)_2L_2$ composition are often formed with either monodentate or bidentate coordination modes of the carboxylate ligands.[6] Low-molecular weight Cu(II) carboxylato compounds have frequently been used to mimic the active site in metalloenzymes, since many metalloprotein active sites have been recognized to have carboxylate-rich coordination environments.[7]

Our interest in these compounds arose from ongoing research on alkyl-chain copper(II) carboxylates with different N-donor ligands that showed increased activity against some wood fungi.[8] We reported recently the synthesis, structures and study of the dimer-monomer equilibrium of copper(II) carboxylates with 2-aminopyridine (2-apy).[6a] In continuation of this work, copper(II) carboxylates with 4-aminopyridine (4-apy) were prepared with attention paid to the influence of the position of the amino group with respect to the pyridine nitrogen atom. Reactions of copper(II) carboxylates with 4-apy resulted in monomeric complexes only, even at low ligand concentrations, presumably due to higher ligand basicity. In this paper, we report the structures of two isomers of the acetate (ac) complex and the structures of the monomeric hexanoate (hex) and heptanoate (hep) complexes, all having $Cu(carboxylate)_2(4\text{-apy})_2$ composition. The acetate isomers exhibit markedly different stability in the solid state. The energy difference between the two isomers was obtained on the basis of an *ab initio* molecular orbital (MO) calculation using the split shell polarization 6-31G* basis set.

We also report the crystal structure of a novel, basic, tetranuclear complex of $Cu_4(oct)_6(OH)_2(4\text{-apy})_2$ composition, with bridging bidentate and monoatomic bridging carboxylate groups, triply bridging hydroxyl groups and terminal 4-aminopyridine ligands.

Experimental

General

Syntheses of the complexes were carried out using commercially available chemicals and solvents. The starting copper(II)

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carboxylates were prepared by the reaction of the appropriate sodium carboxylate in an aqueous solution with the required amount of copper(II) sulfate. So-obtained copper(II) carboxylates were purified by recrystallization from methanol.

IR spectra were recorded on a Perkin–Elmer 1720X spectrophotometer in the region between 4000 and 400 cm^{-1} using nujol and poli oil techniques. Solid state (Nujol mull) UV-VIS spectra were recorded on a Perkin–Elmer Lambda 19 spectrophotometer. Spectra of compounds **1**–**4** can be obtained from the authors upon request. Due to the very low yield, no spectroscopic data are available for compond **5**.

Preparations

Cu(ac)$_2$(4-apy)$_2$, 1. Copper(II) acetate hydrate (0.06 g, 0.15 mmol) was dissolved in 30 mL of acetonitrile, with stirring and heating. 4-Aminopyridine (0.09 g, 1 mmol) was added at the boiling point. An immediate colour change was followed by rapid growth of small, violet, block-shaped crystals from the cooling solution. Maintaining the solution with all the precipitated violet product at room temperature for a month led to the qualitative conversion of the violet form to blue plate-like crystals of Cu(ac)$_2$(4-apy)$_2$, **2**. Yield: 72% (0.08 g). (Found: C, 45.12; H, 4.91; N, 15.15; $C_{14}H_{18}CuN_4O_4$ requires: C, 45.46; H, 4.91; N, 15.15%).

Cu(hex)$_2$(4-apy)$_2$, 3 and Cu(ac)$_2$(4-apy)$_2$, 4. The 4-aminopyridine ligand (0.5 mmol, 0.05 g) was dissolved in the boiling acetonitrile solution containing 0.1 mmol of the corresponding copper(II) carboxylate. The resulting intensely blue solution was filtered to remove any solids and allowed to cool to ambient temperature. On standing (1–2 days) small violet crystals formed. Yield: 62% (0.06 g) average for **3**, 67% (0.07 g) for **4**. (Found for **3**: C, 54.67; H, 7.23; N, 11.80; $C_{22}H_{34}CuN_4O_4$ requires: C, 54.81; H, 7.11; N, 11.62; found for **4**: C, 56.54; H, 7.68; N, 11.07; $C_{24}H_{38}CuN_4O_4$ requires: C, 56.51; H, 7.51; N, 10.98%).

Cu$_4$(oct)$_6$(OH)$_2$(4-apy)$_2$, 5. Cu(II) octanoate (0.09 g) was dissolved in 30 ml of acetonitrile and filtered. The solution of 4-aminopyridine (0.05 g) in a mixture of acetonitrile and water (4 ml, 2 ml) was then added. The resulting turquoise solution was then left at ambient temperature. Blue plate-like single crystals deposited over a month. Yield: 7% (0.04 g). (Found: C, 52.20; H, 7.95, N, 4.24; $C_{58}H_{104}Cu_4N_4O_{14}$ requires: C, 52.16; H, 7.85; N, 4.19%).

Structure determinations

Data were collected on a Nonius Kappa CCD diffractometer using COLLECT[9] and reduced using DENZO.[10] All structures were solved by routine direct methods and refined by least squares refinement on F^2 values.[11] All non-hydrogen atoms were refined anisotropically. Constrained riding hydrogen atoms were included. Crystal data are summarized in Table 1. For structure **1** the absolute structure parameter indicated a racemic twinning of the crystals. Refinement of the racemic twin model resulted in better R values [Flack parameter 0.51(6)]. Problems were encountered with the structure of **5**. The values of R_1 and wR_2 for least squares refinement on F^2 are larger than those normally obtained for small inorganic molecules. This is presumably a consequence of having disordered octanoate alkyl chains. The disorder of one of the three crystallographically independent octanoate groups was successfully resolved. However, the thermal displacement parameters of the carbon atoms of the other two octanoate ligands indicate possible disorder as well. Despite the relatively poor agreement factors, the crystal structure of **5** is conclusive as to the general shape of the molecule.

CCDC reference number 181545. See http://www.rsc.org/suppdata/nj/b1/b110051c/ for crystallographic data in CIF or other electronic format.

Powder diffractogram of compound **1** (after transformation of the violet crystals into a blue powder) was obtained by the Guinier de-Wolf camera (Enraf-Nonius) using Cu-Kα radiation. For comparison of the results with the diffractogram of compound **2**, the interplanar spacings and their relative intensities were calculated using the single-crystal X-ray data for compound **2**.[12]

Computational

To find the energy difference between the two isomers of the monomeric acetate complex, *ab initio* MO calculations at the HF/6-31G* level were performed. The Gaussian 98 suite of programs was used.[13] No geometry optimization was applied. Atomic coordinates were taken as those obtained by the single crystal X-ray diffraction method.

Table 1 Summary of crystal data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{14}H_{18}CuN_4O_4$	$C_{14}H_{18}CuN_4O_4$	$C_{22}H_{34}CuN_4O_4$	$C_{24}H_{38}CuN_4O_4$	$C_{58}H_{104}Cu_4N_4O_{14}$
M	369.86	369.86	482.07	510.12	1335.61
T/K	200	200	200	200	200
Crystal system	Tetragonal	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$I4_1cd$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	8	4	1	1	1
a/Å	10.6062(2)	9.7290(2)	8.6601(4)	8.7347(3)	9.7197(3)
b/Å	—	9.1500(2)	9.2451(4)	9.3621(3)	10.3927(3)
c/Å	31.1002(8)	18.4912(2)	9.3080(4)	9.2479(3)	19.0069(6)
α/°	—	—	75.641(3)	76.727(2)	88.802(1)
β/°	—	94.397(1)	69.130(2)	73.418(2)	84.612(1)
γ/°	—	—	64.620(2)	64.590(2)	68.313(1)
V/Å^3	3498.5(1)	1643.3(3)	625.11(5)	649.65(4)	1776.0(1)
μ/mm^{-1}	1.272	1.355	0.906	0.876	1.238
Coll. reflect.	3123	6111	5264	5042	10 631
Indep. reflect.	1722	3239	3104	2652	6029
R_{int}	0.010	0.025	0.031	0.020	0.063
Obd. reflect. [$I > 2\sigma(I)$]	1466	2711	2184	2464	3986
R_1 [$I > 2\sigma(I)$]	0.042	0.030	0.049	0.031	0.107
wR_2 [$I > 2\sigma(I)$]	0.129	0.087	0.094	0.068	0.284

Results and discussion

Although the amino group of the 4-apy ligand is a potential electron donor, there have been no structures reported with 4-apy as a bridging ligand. In many structures 4-apy exists as the 4-aminopyridinium cation.[14] Only four structures are known in which 4-apy is coordinated to Cu^{2+} ion as a coligand with carbonate,[15] phenanthroline,[16] bis(2-aminoethyl)oxamide[17] and formate.[18] The latter includes carboxylate ion (formate) as a bridging ligand. The result is a polymeric structure with $[Cu(formate)_2(4\text{-}apy)_2]_n$ composition. Analogously to these reports, 4-aminopyridine is a terminal ligand in all five structures reported here.

Two isomers of $Cu(ac)_2(4\text{-}apy)_2$, 1 and 2

The first step of the reaction of copper(II) acetate hydrate with 4-apy in various solvents (acetonitrile, methanol, ethanol, acetone) always produces small violet block-shaped crystals **1**, very unstable when taken from the mother liquor. These crystals transform into a blue powder in less than a minute. The crystal structure of the violet compound revealed the $Cu(ac)_2(4\text{-}apy)_2$ stoichiometry with the ligands arranged around copper ion in the *trans* configuration (Fig. 1).

After storing the solution with the precipitated violet product at room temperature for a month, the conversion of the violet form to blue was completed. The crystals of the blue form are stable in air. On the basis of the elemental analysis the same stoichiometry was proposed as in **1**. It was first erroneously assumed that the blue complex possesses the *cis* geometry, since the colour of the crystals is similar to the colour of monomeric *cis* complexes of copper(II) carboxylates with 2-aminopyridine.[6a] However, the crystal structure showed a *trans* arrangement for the blue compound as well, but with different orientations of the ligands (Fig. 2). In the violet form, **1**, the two 4-apy ligands lie almost in a plane (eclipsed conformer), while they are twisted with respect to each other in the blue form, **2** (staggered conformer). In the eclipsed form, **1**, the copper ion lies on a twofold axis passing through atoms of the 4-apy ligands (N1, C4, N11 and N1′, C4′ and N11′). The basic coordination geometry is planar, and the acetate anions are coordinated in a monodentate fashion [Cu–O11, 1.951(2) Å]. The remaining acetate oxygen atoms are located above and below the plane at longer distances [Cu–O12, 2.810(2) Å] and thus complete the distorted square bipyramidal coordination, most typical for related $Cu(ac)_2L_2$ complexes. Discrete monomeric units of **1** form a three-dimensional network *via* hydrogen bonds through amino nitrogen atoms and non-coordinated acetate oxygen atoms of the neighbouring molecules.

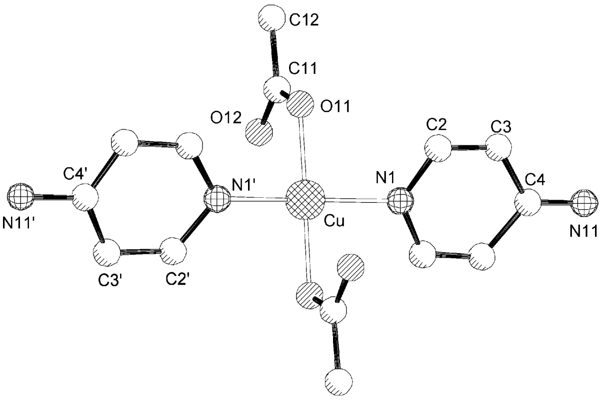

Fig. 1 Molecular structure of $Cu(ac)_2(4\text{-}apy)_2$, **1**, with the atomic numbering scheme.

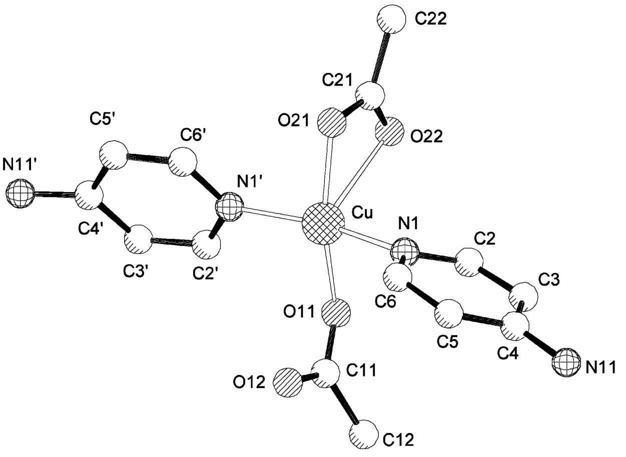

Fig. 2 Molecular structure of $Cu(ac)_2(4\text{-}apy)_2$, **2**, with the atomic numbering scheme.

In the blue, staggered form, **2**, the arrangement of ligands around the copper atom remains trans, but the geometry of the molecule differs from the eclipsed form in many ways. The pyridine rings are twisted, the dihedral angle between the rings being 61.60(7)°. In the perpendicular direction two crystallographically independent acetate groups are coordinated to copper ion with a mutual angle of 23.6(3)°. While in the eclipsed form the coordination is essentially planar with two acetate oxygen atoms above and below the plane, the coordination in the staggered form deviates from the planar arrangement. One of the acetate ligands (O11, O12, C11 and C12) is coordinated as monodentate with a Cu–O11 distance of 1.9446(14) Å . O12 is located at a distance of 3.1274(17) Å from the copper atom, which is even longer than the corresponding distance in the eclipsed form. The second acetate group is coordinated in a bidentate fashion with the distances Cu–O21 and Cu–O22 being 2.0102(14) and 2.4845(16) Å, respectively. The resulting coordination is square pyramidal. The value of the parameter τ, introduced to describe the degree of trigonality,[19] is in our case 0.049. For a perfectly tetragonal geometry τ is equal to zero, while it becomes unity for a perfectly trigonal-bipyramidal geometry. The basal plane is formed by N atoms of two 4-apy ligands and by O atoms of the two acetate groups (O11 and O21). The apical position is occupied by the second oxygen atom of one of the acetate groups (O22). Thus, the isomerism found for the two forms could be described as coordinational, rather than simply rotational. A perspective view of the two isomers is presented in Fig. 3. Selected geometrical parameters are presented in Table 2.

The two isomers exhibit markedly different stabilities. Crystals of the violet form, **1**, decompose rapidly into a blue powder after removal from the mother liquor. It was proposed that the violet form transforms into the blue one, which was further confirmed by X-ray powder diffraction. The measured powder diffractogram of the decomposed sample of **1** was identical to the calculated one of the staggered form, **2**, based on the single crystal X-ray structure.

Since there is a difference in coordination mode of the carboxylate ligands to the copper centre, a larger energy difference between the isomers than that for rotational isomerism was expected. The calculated energy difference ΔE is 376.6 kcal mol^{-1} ($E_{staggered} < E_{eclipsed}$) and corresponds to the formation of an additional coordination bond between Cu and O22 in the staggered form. Although the calculated value of the energy difference is too high (if only the formation of an additional coordination bond is taken into account), it definitely shows that one of the isomers is energetically more favoured. The

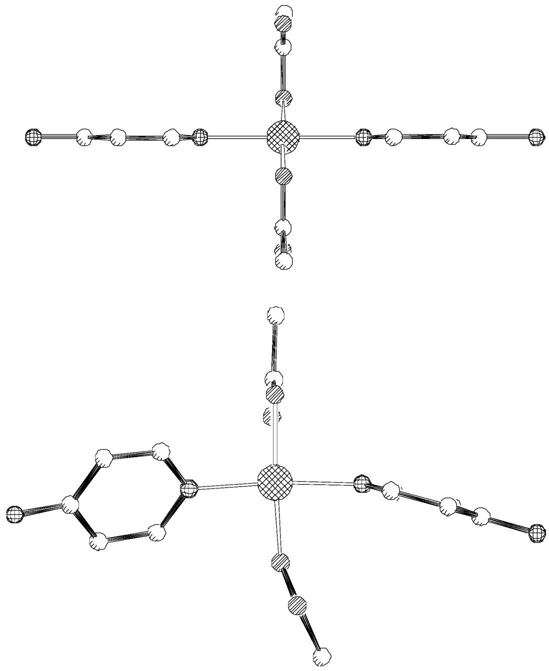

Fig. 3 Perspective view of the two isomers of $Cu(ac)_2(4\text{-}apy)_2$ showing the orientation of the acetate and 4-aminopyridine ligands. Eclipsed form, **1**, (top) and staggered form, **2**, (bottom).

Table 2 Selected geometrical parameters (Å, °) for compounds **1** and **2**

	1	2
Cu–N1	2.075(15)	1.9968(16)
Cu–N1′	1.928(2)	1.9846(17)
Cu–O11	1.951(2)	1.9446(14)
Cu–O12	2.809(2)	3.1274(17)
Cu–O21	—	2.0102(14)
Cu–O22	—	2.4845(16)
O11–Cu–N1	90.2(3)	87.09(7)
O11–Cu–N1′	89.2(3)	92.36(7)
N1–Cu–N1′	180.0	167.14(7)
O11–Cu–O21	—	164.20(6)
O11–Cu–O22	—	95.74(7)

change of the coordination number from four to five obviously stabilizes the complex.

Structures of $Cu(hex)_2(4\text{-}apy)_2$, 3, and $Cu(hep)_2(4\text{-}apy)_2$, 4

Mononuclear copper(II) hexanoate and heptanoate complexes with 4-apy are isostructural. The geometry of the molecules in these two complexes is typical and most often observed for monomeric copper(II) carboxylates. Copper ion occupies a centre of symmetry and is surrounded by N atoms (N1) from the two 4-apy ligands and O atoms (O11) from each of the two carboxylate ligands, resulting in a *trans* square-planar configuration. Similar as in the eclipsed form of the acetate complex, the remaining two coordination positions above and below the plane are blocked by carboxylate oxygen atoms (O12), located at longer distances. The dihedral angle between the planes of the 4-apy ligands and carboxylate groups are 82.6(2) and 82.72(15)° for the hexanoate and heptanoate structures, respectively. Selected geometrical parameters are quoted in Table 3. The alkyl chains in both complexes involve a gauche relation at the C12–C13 bond, giving a torsion angle C11–C12–C13–C14 of −65.8(5)° for **3** and −65.1(2)° for compound **4**. After the gauche relation the hydrocarbon chains are in a planar *trans* extended conformation and are oriented almost parallel to the 4-apy rings (Fig. 4).

Table 3 Selected geometrical parameters (Å, °) for compounds **3** and **4**

	3	4
Cu–N1	1.9890(18)	1.9847(14)
Cu–O11	1.9985(19)	1.9717(12)
Cu–O12	2.628(2)	2.6247(13)
O11–C11	1.288(4)	1.271(2)
O12–C11	1.255(5)	1.247(2)
N1–Cu–O11	90.19(8)	90.13(5)
N1–Cu–O12	94.01(8)	94.21(5)
O11–Cu–O12	55.60(9)	55.33(5)

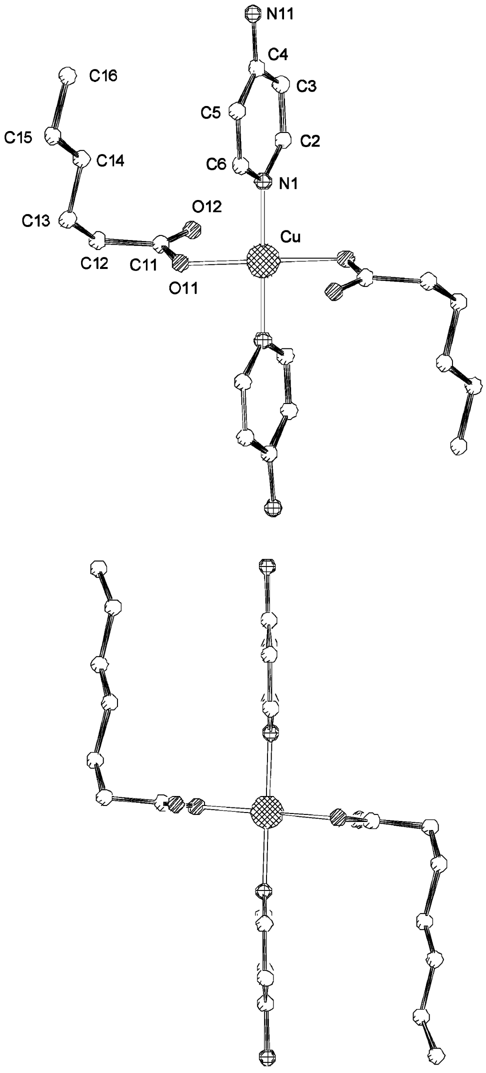

Fig. 4 Molecule of $Cu(hex)_2(4\text{-}apy)_2$, **3**, with the atomic numbering scheme (top) and perspective view (bottom) of $Cu(hep)_2(4\text{-}apy)_2$, **4**, showing the parallel orientation of the carboxylate alkyl chains to the pyridine rings.

As expected, amino groups are involved in a hydrogen bond formation. The *para* position of the amino group with respect to the pyridine N atom precludes any intramolecular hydrogen bonding. A two-dimensional network, parallel to the *ab* plane, is created *via* intermolecular H bonds to non-coordinated carboxylate oxygen atoms of the neighbouring monomeric units.

Structure of $Cu(oct)_6(OH)_2(4\text{-}apy)_2$, 5

The structural analysis has shown the blue crystals of compound **5** to be composed of discrete centrosymmetric molecules. A view of the structure of a tetranuclear molecule is presented in Fig. 5 and selected geometrical parameters in Table 4. The two crystallographically independent copper ions possess distorted square pyramidal coordination. Three independent octanoate groups are present in the molecule; two of them form bridges from the basal position of one copper ion to the basal site of the second copper ion. The third octanoate anion is bound as a monoatomic bridging ligand to the apical position, shared by both polyhedra. 4-Aminopyridine is coordinated to Cu1 only and occupies one of the basal positions. The dihedral angle between the Cu1 and Cu2 basal planes is 63.3(2)° with the displacement of copper atoms of 0.122(3) (Cu1) and 0.180(2) Å (Cu2) from the basal plane toward the apical position. The distance between the symmetry related hydroxo-bridged Cu2 atoms is 2.894(2) Å, while the separations between Cu1 and Cu2 are larger. Cu1 and Cu2, bridged through carboxylate group 2, are separared by 3.0769(16) Å. The distance between Cu1 and Cu2 (at $-x$, $-y+1$, $-z+1$), separated by carboxylate group 1, is 3.3092(15) Å. These distances are much longer than the average Cu···Cu separation reported for tetracarboxylato bridged dimeric compounds (2.676 and 2.625 Å for CuO_4O and CuO_4N chromophores, respectively.)[4b] Basic Cu(II) carboxylates are known, but none of the reported examples showed a stoichiometry resembling this structure. The closest example is the structure of the basic tetranuclear quinoline adduct of copper trifluoroacetate with a $Cu_4(tfc)_6(OH)_2(quin)_4$ stoichiometry.[20] One molecule contains two crystallographically independent Cu ions, bridged by two independent carboxylate ligands. Similarly, the coordination geometry around each copper atom is square pyramidal. The third carboxylate group is monodentate, bound only to one of the copper atoms at the basal position, while in our case the third carboxylate group forms a monotomic bridge between the two copper atoms and thus represent the common edge of the coordination polyhedra. In the previously reported tetramer, bridging carboxylate groups connect the basal position of one copper atom with the apical position of the other. Quinoline ligands are bound to each of the copper ions, while in the herein reported structure only one of the two copper atoms is coordinated by 4-aminopyridine. In both compounds triply bridging hydroxide groups are observed.

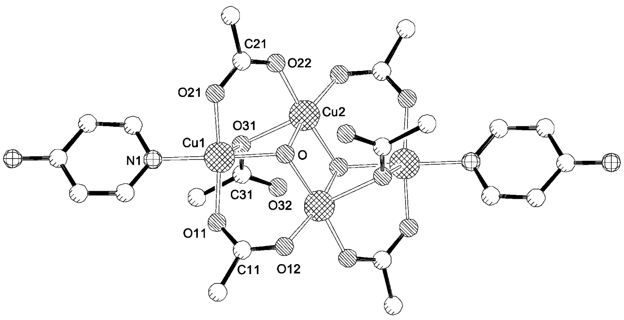

Fig. 5 View of the molecular structure of **5**. For clarity, carbon atoms of the octanoate alkyl chains are omitted.

Table 4 Selected geometrical parameters (Å, °) for compound **5**

Cu–O	1.977(6)	Cu2–O	2.021(7)
Cu1–N1	2.032(8)	Cu2–O^i	1.923(7)
Cu1–O21	1.974(7)	Cu2–O22	1.933(7)
Cu1–$O11^i$	1.937(7)	Cu2–O12	1.951(7)
Cu1–O31	2.450(7)	Cu2–O31	2.333(7)
Cu1–O–Cu2	100.6(3)	$Cu2^i$–O–Cu1	116.1(4)
$Cu2^i$–O–Cu2	94.4(3)		

Symmetry operator *i*: $-x$, $-y+1$, $-z+1$.

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